

# PATENT ABSTRACTS OF JAPAN

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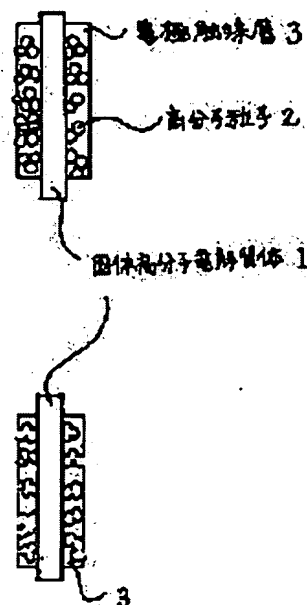
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## (54) SOLID POLYMER FUEL CELL AND MANUFACTURE THEREOF

### (57)Abstract:

**PURPOSE:** To provide a cell of a solid polymer fuel cell with high output by increasing porosity of an electrode catalyst layer and enhancing reaction gas distributing capability.

**CONSTITUTION:** When an electrode catalyst layer 3 is formed on a solid polymer electrolyte film 1, by using dispersion plating relating to chemical plating, an electrode catalyst salt is adsorbed together with polymer particles 2, then the polymer particles 2 are removed in an acidic solution to obtain a porous electrode catalyst layer 3. Or porous organic polymer resin is formed on the solid polymer electrolyte film 1, then chemical plating is conducted to form the electrode catalyst layer on the surface of the porous organic polymer resin layer, or on the surfaces of the porous organic polymer resin layer and the solid polymer electrolyte film 1.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the improvement in a property of a cel with respect to a polymer electrolyte fuel cell and its manufacture approach.

[0002]

[Description of the Prior Art] A fuel cell is divided roughly into a polymer electrolyte fuel cell, a phosphoric acid mold fuel cell, a fused carbonate fuel cell, a solid oxide fuel cell, etc. by the electrolytic class and the operating temperature which are used for this. The polymer electrolyte fuel cell has the description which high power density is obtained since the differential pressure control between two electrodes and pressurization-izing of a cell are easy compared with other fuel cell systems, and can use carbon-dioxide content gas as it is since it is an acid electrolyte object. Since it is furthermore a low-temperature actuation mold, there is little constraint in respect of a cell component, and it can start in ordinary temperature in a short time.

[0003] The basic configuration of a polymer electrolyte fuel cell cel is shown in drawing 6 . A cell 8 has anode 74a and cathode 74b to both sides of the solid-state polyelectrolyte object 7, and possesses electrode substrates 75a and 75b to the outside both sides. Furthermore that outside is \*\*\*\*(ed) by the separators 76a and 76b of gas impermeability, this separator 76a has fuel gas flowing path 29a, and separator 76b has oxidizer gas conduction way 29b.

[0004] the fuel gas and oxidizer gas which were supplied to the cel are consumed by the following electrochemical reaction in the three-phase zone formed with each electrode catalyst bed and a solid-state polyelectrolyte object -- having -- as a whole reaction -- water -- generating -- moreover, a proton -- a solid-state polyelectrolyte -- in order to move in the state of hydration in the inside of the body, water generates in a cathode.

[0005]

[Formula 1]

$H_2 \rightarrow 2H^{++} + 2e^-$  Anode [0006]

[Formula 2]

(1/2)  $O_2 + 2H^{++} + 2e^- \rightarrow H_2O$  As a cathode solid-state polyelectrolyte object 7 The hydrophobic principal chain this cation exchange membrane of whose the perfluoro sulfonic acid resin film (for example, the U.S. Du Pont make, trade name Nafion) which has resistance in oxidization or heat is used, and is a carbon fluoride system macromolecule, Consisting of an exchange group of the hydrophilic property which is the side chain which consists of carbon fluoride which has a sulfone radical at a tip, this exchange group meets in a fluorocarbon matrix, and forms the cluster. By making saturation carry out water to a cluster part, in ordinary temperature, this solid-state polyelectrolyte 7 shows the specific resistance of 20 or less ohm-cm, and functions as a proton conductor and a gas separator. Therefore, after humidifying reactant gas beforehand, it is supplied to a cel.

[0007] Since an electrode catalyst bed touches the solid-state polyelectrolyte object which is strong corrosive acidity, a catalyst is limited to noble metals, such as platinum, and CO becomes catalyst poison. The function of the electrode catalyst bed in a fuel cell has the function as a gas diffusion electrode which supplies gas and takes out a lifting direct current for electrochemical reaction. That is, for improvement in a cel property, it is required that the electrode catalyst bed has the moderate

hole and for the three-phase zone which is the place of a reaction to be large.

[0008] By the former, after applying the mixed solution of the carbon and polytetrafluoroethylene which made platinum support, drying and heating it and forming an electrode catalyst bed on the carbon-electrode base material of a conductive porous body, the cel of such a polymer electrolyte fuel cell carries out the hotpress of this electrode catalyst bed side to both the principal planes of a solid-state polyelectrolyte object, and is obtained. However, a large three-phase zone cannot be easily acquired by the cel obtained by doing in this way, and it has the fault that a solid-state polyelectrolyte object receives breakage partially with compressive stress. Furthermore, increase of the manufacturing cost by enlargement of an application device is accompanied by large area-ization of a plane of composition.

[0009] In order to solve these, chemistry plating which forms a platinum catalyst layer by the thing which made platinate stick to both the principal planes of the solid-state polyelectrolyte object which pretreated, and to do for post reduction, and forms the cel which has a large three-phase zone comparatively cheaply and easily is tried. Although pore is formed since the gas which occurred in the solid-state polyelectrolyte body in the above-mentioned reduction process is discharged out of a system, the electrode catalyst bed still obtained by chemistry plating has the fault that porosity is low and the function as a gas diffusion electrode and a generation-of-gas electrode is checked.

[0010]

[Problem(s) to be Solved by the Invention] In the above, although the three-phase zone of reactant gas, an electrode catalyst bed, and a solid-state polyelectrolyte object is formed, since the electrode catalyst bed obtained by chemistry plating is precise, it runs short of porosity, and has the fault that the mutual diffusibility of reactant gas is low. That is, the amount of the catalyst which the reactant gas which has diffused the inside of an electrode substrate cannot fully be spread inside an electrode catalyst bed, but contacts reactant gas, and can contribute to a reaction will be restricted.

[0011] This invention aims at offering the possible polymer electrolyte fuel cell and its manufacture approach of high power with the high diffusibility of reactant gas.

[0012]

[Means for Solving the Problem] The cel which generates direct current power in response to supply of fuel gas and oxidizer gas first the above-mentioned purpose A solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Said cel is attained in an electrode substrate and the manufacture approach of the polymer electrolyte fuel cell which two or more laminatings are further carried out through a separator, and constitutes a cell accumulation object (stack) by forming an electrode catalyst bed on a solid-state polyelectrolyte object with distributed plating concerning chemistry plating.

[0013] In the manufacture approach of the above-mentioned polymer electrolyte fuel cell moreover, distributed plating It has the 1st process, the 2nd process, and the 3rd process. The 1st process An electrode catalyst salt is made to stick to a solid-state polyelectrolyte object with a macromolecule particle, the 2nd process returns the solid-state polyelectrolyte object which adsorbed this electrode catalyst salt and the macromolecule particle, and forms an electrode catalyst bed, and the 3rd process is immersed in an acidic solution and attained by removing said macromolecule particle.

[0014] Moreover, in the manufacture approach of the above-mentioned polymer electrolyte fuel cell, the giant-molecule particle used with distributed plating is attained by being one in the group which consists of a butadiene, acrylic resin, polyurethane, phenol resin, and melamine resin. The cel which generates direct current power in response to supply of fuel gas and oxidizer gas Furthermore, a solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. In an electrode substrate and the polymer electrolyte fuel cell which two or more laminatings are further carried out through a separator, and constitutes a cell accumulation object (stack), said cel is the porous film and the pore size said electrode catalyst bed It is attained by considering as the range of 0.1 micrometers thru/or 10 micrometers.

[0015] The cel which generates direct current power in response to supply of fuel gas and oxidizer gas Furthermore, a solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte

object, respectively. Said cell sets to an electrode substrate and the manufacture approach of the polymer electrolyte fuel cell which two or more laminatings are further carried out through a separator, and constitutes a cell accumulation object (stack). It has the 1st process and the 2nd process. The 1st process A porous organic macromolecule resin layer is formed on both the principal planes of a solid-state polyelectrolyte object, and the 2nd process is attained by forming an electrode catalyst bed with chemistry plating on the front face of said porous organic macromolecule resin layer, or a porous organic macromolecule resin layer and the front face of a solid-state polyelectrolyte object.

[0016] Moreover, in the manufacture approach of the above-mentioned polymer electrolyte fuel cell, it is attained by using polyurethane foam for a porous organic macromolecule resin layer. The cell which generates direct current power in response to supply of fuel gas and oxidizer gas Furthermore, a solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Two or more laminatings are further carried out through a separator, and said cell sets to an electrode substrate and the polymer electrolyte fuel cell which constitutes a cell accumulation object (stack). It is attained by forming said electrode catalyst bed on the front face of said porous organic macromolecule resin layer, or a porous organic macromolecule resin layer and the front face of a solid-state polyelectrolyte object.

[0017]

[Function] Porosity is obtained enough and, as for an electrode catalyst bed, reactant gas becomes easy to diffuse the inside of an electrode catalyst bed. Consequently, since the touch area of reactant gas, an electrode catalyst bed, and a solid-state polyelectrolyte object becomes large and a big three-phase zone is acquired, in a polymer electrolyte fuel cell, high power becomes possible.

[0018]

[Example] Hereafter, the example of this invention is explained with reference to a drawing.

Example 1; drawing 1 is one example of the manufacture approach of the polymer electrolyte fuel cell of this invention concerning claims 2, 3, and 4, and they are the mimetic diagram having shown the condition that drawing 1 R> 1 (a) carried out distributed plating to the solid-state polyelectrolyte object, and the mimetic diagram having shown the condition of drawing 1 (b) having removed the macromolecule particle and having formed the porous electrode catalyst bed.

[0019] In drawing 1 (a), the solid-state polyelectrolyte object 1 is first pretreated with the acid solution which is for example, a sulfuric-acid water solution. It sets to the jig 31 made of acrylic resin which shows this solid-state polyelectrolyte object 1 to drawing 2. For 31, as for a locking bolt and 33, in drawing 2, the jig for plating made of acrylic resin and 32 are [ silicone rubber packing and 34 ] liquid rooms. Next, the solution which distributed the macromolecule particle 2 of a butadiene in the aqueous ammonia solution of a platinum catalyst is poured in into the liquid room 34, and is heated, and the platinate of the specified quantity is made to stick to both the principal planes of the solid-state polyelectrolyte object 1. Next, the reducing agent which is the aqueous ammonia solution of the sodium borohydride which distributed the macromolecule particle 2 is filled and heated in the liquid room 34, and the electrode catalyst bed 3 which is the platinum metal which returned platinate and included the macromolecule particle 2 is obtained. After rinsing enough, it processes with the acid solution which is a sulfuric acid, only the macromolecule particle 2 is removed, and the porous electrode catalyst bed 3 as shown in drawing 1 (b) is obtained. As a giant-molecule particle, acrylic resin, polyurethane, phenol resin, melamine resin, etc. can be used in addition to the above-mentioned butadiene.

[0020] the particle size of the macromolecule particle 2 used for the pore size of the obtained porous electrode catalyst bed 3 -- control -- possible -- 0.1  $\mu\text{m}$  from -- 10  $\mu\text{m}$  up to -- it is producible. In addition, as a giant-molecule particle used with distributed plating, acrylic resin, polyurethane, phenol resin, melamine resin, etc. may be used in addition to the above-mentioned butadiene.

Example 2; drawing 3 is one example of the manufacture approach of the polymer electrolyte fuel cell of this invention concerning claims 5 and 6, and the mimetic diagram and drawing 3 (b) which showed the condition that drawing 3 (a) made the porosity organic macromolecule resin layer bind to a solid-state polyelectrolyte object are the mimetic diagram having shown the condition of having formed the electrode catalyst bed with chemistry plating on the front face of the porous organic

macromolecule resin layer 4.

[0021] In drawing 3 (a), first mix the ORGANO silicon which is the polyisocyanate which is the raw material of porous organic macromolecule resin, the chlorofluocarbon which is polyol and a firing agent, and a foam stabilizer, and supply amines there, a polyaddition reaction is made to start, and it is made the shape of an opaque cream. This is applied to the solid-state polyelectrolyte object 1, and it is made to bind on a solid-state polyelectrolyte object at the same time it keeps at 50 degrees C and forms the porous organic macromolecule resin layer 4. Next, it sets to the jig 31 for plating made of acrylic resin shown in drawing 2 like an example 1, after ionizing the front face of the porous organic macromolecule resin layer 4 using tin chloride. The aqueous ammonia solution of a platinum catalyst is poured in into the liquid room 34, and is heated, and the platinate of the specified quantity is made to stick to the front-face top of the porous organic macromolecule resin layer 4, or the front face of the porous organic macromolecule resin layer 4 and the solid-state polyelectrolyte object 1. Next, the reducing agent which is the aqueous ammonia solution of a sodium borohydride is filled and heated in the liquid room 34, and platinate is returned, it considers as a platinum metal, and the electrode catalyst bed 3 as shown in drawing 3 (b) is obtained.

[0022] Example 3; drawing 4 is an example from which the manufacture approach of the polymer electrolyte fuel cell of this invention concerning claims 5 and 6 differs, and the mimetic diagram and drawing 4 (b) which showed the condition that drawing 4 (a) made the porosity organic macromolecule resin layer bind to a solid-state polyelectrolyte object are the mimetic diagram having shown the condition of having formed the electrode catalyst bed with chemistry plating on the porous organic macromolecule resin layer 4 and the front face of the solid-state polyelectrolyte object 1. In addition, the same sign is given to the same part as the mimetic diagram shown in drawing 3.

[0023] It differs from drawing 3 (b) in that drawing 4 (b) formed the electrode catalyst bed on the porous organic macromolecule resin layer 4 and the front face of the solid-state polyelectrolyte object 1. About what included the cel produced in the examples 1 and 2 in the cell, and constituted it, the current potential property is measured and the result compared with the conventional thing is shown in drawing 5. In drawing 5, the current potential property of the cel of the former [ diagram / 11 ], the current potential property of the cel which produced the diagram 12 in the example 1, and a diagram 13 are the current potential properties of the cel produced in the example 2. That is, by using the manufacture approach by this example shows that the gas diffusion electrode function increased and the property in high current density improved remarkably. Moreover, the property improvement with the same said of the cel produced in the example 3 was found.

[0024] In addition, although the above-mentioned publication is related with a polymer electrolyte fuel cell, this invention is applied also to what takes out the gas which occurs in an electrode according to electrochemical reaction like for example, water electrolysis equipment besides this.

[0025]

[Effect of the Invention] In this invention, the high electrode of reactant gas diffusibility becomes possible [ offering the polymer electrolyte fuel cell which is obtained and has the outstanding cel property ] by adopting the above configurations and the manufacture approach.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The cell which generates direct current power in response to supply of fuel gas and oxidizer gas. A solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Said cell sets to an electrode substrate and the manufacture approach of the polymer electrolyte fuel cell which two or more laminations are further carried out through a separator, and constitutes a cell accumulation object (stack). The manufacture approach of the polymer electrolyte fuel cell characterized by forming an electrode catalyst bed on a solid-state polyelectrolyte object with distributed plating concerning chemistry plating.

[Claim 2] In the manufacture approach of a polymer electrolyte fuel cell according to claim 1 distributed plating. It has the 1st process, the 2nd process, and the 3rd process. The 1st process An electrode catalyst salt is made to stick to a solid-state polyelectrolyte object with a macromolecule particle. The 2nd process It is the manufacture approach of the polymer electrolyte fuel cell characterized by returning the solid-state polyelectrolyte object which adsorbed this electrode catalyst salt and the macromolecule particle, forming an electrode catalyst bed, immersing the 3rd process in an acidic solution, and removing said macromolecule particle.

[Claim 3] The giant-molecule particle used with distributed plating in the manufacture approach of a polymer electrolyte fuel cell according to claim 1 is the manufacture approach of the polymer electrolyte fuel cell characterized by being one in the group which consists of a butadiene, acrylic resin, polyurethane, phenol resin, and melamine resin.

[Claim 4] The cell which generates direct current power in response to supply of fuel gas and oxidizer gas. A solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Two or more laminations are further carried out through a separator, and said cell sets to an electrode substrate and the polymer electrolyte fuel cell which constitutes a cell accumulation object (stack). Said electrode catalyst bed is the porous film, and the pore size Polymer electrolyte fuel cell characterized by considering as the range of 0.1 micrometers thru/or 10 micrometers.

[Claim 5] The cell which generates direct current power in response to supply of fuel gas and oxidizer gas. A solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Said cell sets to an electrode substrate and the manufacture approach of the polymer electrolyte fuel cell which two or more laminations are further carried out through a separator, and constitutes a cell accumulation object (stack). It has the 1st process and the 2nd process. The 1st process A porous organic macromolecule resin layer is formed on both the principal planes of a solid-state polyelectrolyte object. The 2nd process The manufacture approach of the polymer electrolyte fuel cell characterized by forming an electrode catalyst bed with chemistry plating on the front face of said porous organic macromolecule resin layer, or a porous organic macromolecule resin layer and the front face of a solid-state polyelectrolyte object.

[Claim 6] The manufacture approach of the polymer electrolyte fuel cell characterized by using polyurethane foam for a porous organic macromolecule resin layer in the manufacture approach of a polymer electrolyte fuel cell according to claim 5.

[Claim 7] The cel which generates direct current power in response to supply of fuel gas and oxidizer gas A solid-state polyelectrolyte object, It has the fuel electrode catalyst bed (anode) and oxidizer electrode catalyst bed (cathode) which were arranged on both sides of this electrolyte object, respectively. Two or more laminatings are further carried out through a separator, and said cel sets to an electrode substrate and the polymer electrolyte fuel cell which constitutes a cell accumulation object (stack). The polymer electrolyte fuel cell characterized by forming said electrode catalyst bed on the front face of said porous organic macromolecule resin layer, or a porous organic macromolecule resin layer and the front face of a solid-state polyelectrolyte object.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram having shown the condition of having been one example of the manufacture approach of the polymer electrolyte fuel cell of this invention, and the mimetic diagram having shown the condition that drawing 1 (a) carried out distributed plating to the solid-state polyelectrolyte object, and drawing 1 (b) having removed the macromolecule particle, and having formed the porous electrode catalyst bed.

[Drawing 2] The mimetic diagram of the jig for plating made of acrylic resin used for manufacture of the polymer electrolyte fuel cell of this invention

[Drawing 3] It is the mimetic diagram having shown the condition that were the example from which the manufacture approach of the polymer electrolyte fuel cell of this invention differs, and the mimetic diagram having shown the condition that drawing 3 (a) made the porosity organic macromolecule resin layer bind to a solid-state polyelectrolyte object, and drawing 3 (b) formed the electrode catalyst bed with chemistry plating on the front face of the porous organic macromolecule resin layer 4.

[Drawing 4] It is the mimetic diagram having shown the condition that were the example from which the manufacture approach of the polymer electrolyte fuel cell of this invention differs further, and the mimetic diagram having shown the condition that drawing 4 (a) made the porosity organic macromolecule resin layer bind to a solid-state polyelectrolyte object, and drawing 4 (b) formed the electrode catalyst bed with chemistry plating on the porous organic macromolecule resin layer 4 and the front face of the solid-state polyelectrolyte object 1.

[Drawing 5] The diagram showing the current potential property of the polymer electrolyte fuel cell concerning the example of this invention as contrasted with the current potential property of the conventional polymer electrolyte fuel cell

[Drawing 6] The mimetic diagram showing the cell configuration of the conventional polymer electrolyte fuel cell

[Description of Notations]

- 1 Solid-state Polyelectrolyte Object
- 2 Macromolecule Particle
- 3 Electrode Catalyst Bed
- 4 Porous Organic Macromolecule Resin Layer
- 5 Electrode Catalyst Bed
- 31 Jig for Plating made of Acrylic Resin
- 32 Locking Bolt
- 33 Silicone Rubber Packing
- 34 Liquid Room
- 8 Cell
- 7 Solid-state Polyelectrolyte Object
- 74a Anode
- 74b Cathode

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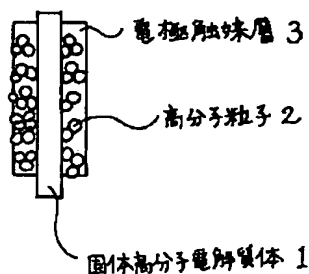
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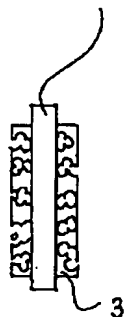
## DRAWINGS

[Drawing 1]

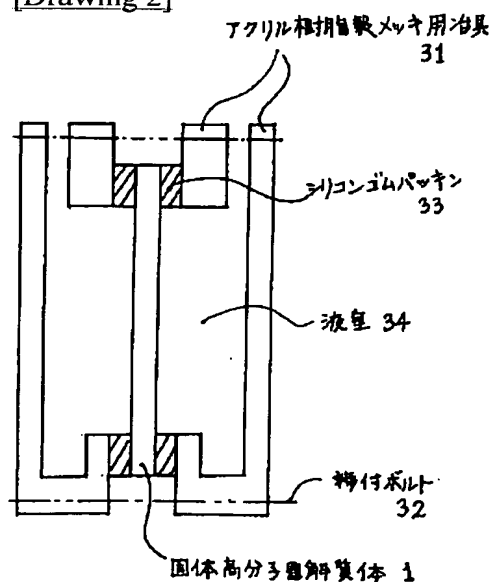
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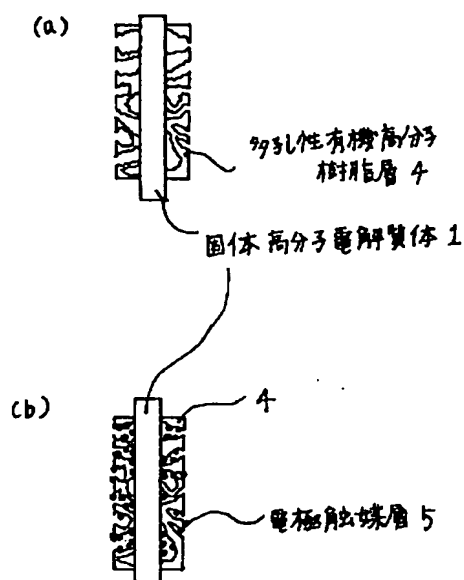
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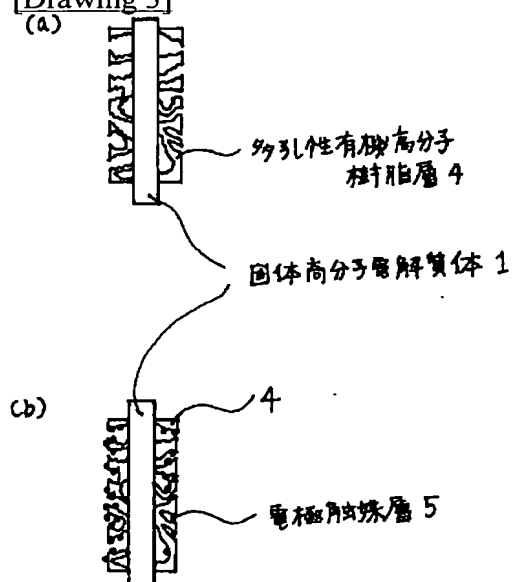
[Drawing 2]



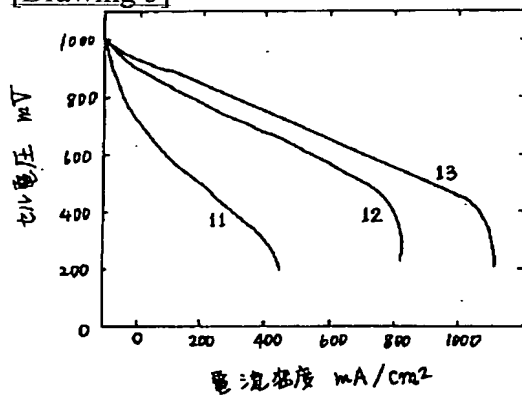
[Drawing 4]



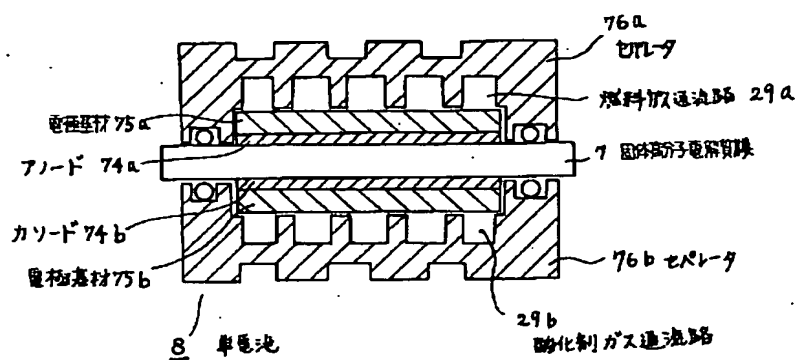
[Drawing 3]



[Drawing 5]



[Drawing 6]



[Translation done.]